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(54) Title: FLUORINATED POLYURETHANE COATED GOLF BALLS

(57) Abstract

The present invention is directed towards golf balls comprising a core, a cover and a coating composition layer, wherein the coating composition layer comprises a fluorinated polyurethane. The novel fluorinated polyurethane coating composition of the present invention enhances a variety of properties such as enhanced abrasion, impact and weathering resistance as compared to golf balls with conventional coating composition. Additionally, the presently claimed fluorinated polyurethane coatings also decrease the coefficient of friction of the surface of the golf ball, resulting in a modification of the spin rate when struck with a golf club and superior cleaning characteristics.

FLUORINATED POLYURETHANE COATED GOLF BALLS

FIELD OF INVENTION

This invention relates generally to a coating for use on golf balls wherein the coating comprises a fluorinated polyurethane. The presently claimed coated objects possess a variety of desirable properties such as enhanced abrasion, impact and weathering resistance to the ball. Additionally, the coatings also decrease the coefficient of friction of the coated surface.

BACKGROUND OF THE INVENTION

Conventional golf balls can be classified as one-piece, two-piece, and three-piece (also known as "wound" balls). One-piece balls are molded from a homogeneous mass of material and have a dimple pattern molded on their surface. Two-piece balls are made by molding a cover about a solid core. Three-piece or wound balls are made by molding a cover about a wound core. The core is typically made of rubber and can be solid, semi-solid or have a liquid center. A wound core is prepared by winding a lengthy thread of elastic material about a solid, semi-solid or liquid center. The wound core is thereafter surrounded with a cover material. A more recent trend in the golf ball art is towards the development of multi-component golf balls such as balls with two or more core layers, two or more cover layers or both multiple core and multiple cover layers.

The covers of presently available golf balls are typically formed from a variety of materials such as balata, polyurethane and ionomer resins such as SURLYN® and IOTEK®, depending upon the desired performance characteristics of the golf ball. One of the softest materials conventionally used in forming golf ball covers is balata, which is the trans form of the 1,4-chain polymer of isoprene. For many years, balata was the standard cover stock material for most golf balls. Balata covered balls are favored among professionals and more advanced amateur players because the softness of the

golf ball is flexed every time it is impacted with a club and consequently it must be able to withstand repeated stresses without damage to the cover. Moreover, especially with the recreational player, golf balls are susceptible of striking any of a number of hard, abrasive surfaces such as concrete, asphalt, brick, stone, and the like as a result of errant shots and their resistance to such impact and abrasion is another important feature.

Naturally, it is further desirable for golf ball manufacturers that their golf balls be resistant to delamination or chipping of the paint layers, as such aesthetic defects impact negatively upon the public perception of the quality of the golf ball. Likewise, golf ball manufacturers prefer to prevent obliteration of all or part of their trademarks, logos or other identifying indicia which identifies the brand of the ball to the playing public.

Conventionally, coating compositions are applied to the ball surface to protect the ball, the identifying indicia and any paint layers, and to add a pleasing appearance to the ball due to their high gloss and the mirror-like surface they produce. Typically, such coatings comprise a clear primer coat and a clear top coat, although for certain applications a single coating composition layer may suffice.

The term "coating composition", as used herein, means a coating applied to the outer surface of the golf ball which is transparent and which imparts a glossy or shiny appearance to the coated surface, as well as providing a measure of protection and durability thereto. Coating compositions are generally free of pigmentation and are water white. However, they may contain small amounts of dye, pigment, and optical brighteners. In golf balls of the type described above, the various identifying indicia may be applied to either the cover, the prime coat or the coating composition.

Protective coating composition materials are well known in the golf ball art. Generally, they consist of urethanes, urethane hybrids, polyesters and acrylics. In

reduced coefficient of friction of the surface of golf balls having such coatings.

The present invention is further directed towards fluorinated polyurethane coating compositions having a plurality of poly(tetrafluoroethylene) particles dispersed therein.

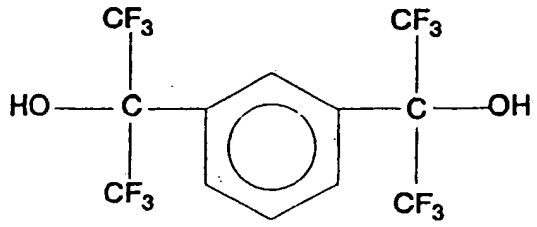
In a further embodiment, the invention is directed towards a golf ball comprising a core, a cover and a coating composition layer upon at least a portion of an outer surface of said cover, wherein the coating composition layer comprises a fluorinated polyurethane coating composition comprised of a reaction product of a fluorinated polyol and a curing agent, preferably an isocyanate.

The present invention is still further directed towards a method for making a golf ball having a coating composition layer comprising a fluorinated polyurethane coating composition formed by a method comprising reacting at least two diols, wherein the diols are either both fluorinated or one is fluorinated and the other is unfluorinated, to form a fluorinated polyol, optionally dispersing the fluorinated polyol in a solvent, adding a curing agent to the polyol/solvent mixture or neat polyol, depositing the polyol/solvent/curing agent mixture or neat polyol/curing agent mixture onto the outer surface of a golf ball and curing the mixture to form a fluorinated polyurethane.

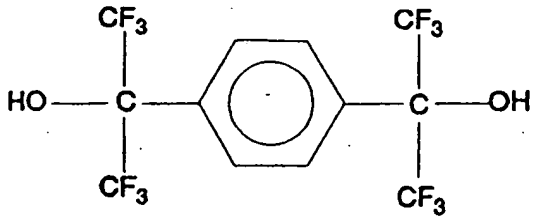
The present invention is yet further directed towards a golf ball having a coating composition layer comprising a fluorinated polyurethane, wherein the fluorinated polyurethane is created by reacting at least two diols, wherein the diols are either both fluorinated or one is fluorinated and the other is unfluorinated, to form a fluorinated polyol, optionally dispersing the fluorinated polyol in a solvent, adding a curing agent to the polyol/solvent mixture or neat polyol, depositing the polyol/solvent/curing agent mixture or neat polyol/curing

The fluorinated polyurethane coating compositions used in the present invention can be formed by the reaction of a fluorinated polyol and a curing agent or by any other method known to the artisan of ordinary skill. A variety of fluorinated polyols may be chosen for reaction with the curing agent, as would be readily apparent to one of ordinary skill in the art. Such fluorinated polyols can be derived from a variety of fluorinated diols. Substantially any fluorinated diols, such as aromatic, unsaturated and aliphatic diols, may be employed to produce the fluorinated polyols employed in the present invention as a coating for the balls. As for the curing agent, any curing agent known in the art for curing urethanes can be used, with isocyanates being the preferred class of curing agents for this purpose.

In a preferred embodiment of the invention, diols having the following chemical structures are preferred for forming the fluorinated polyols used in forming the coated balls of the invention:



(I)



(II)

wherein R_2, R_3 and R_4 are each selected from the group consisting of diols, with the provision that at least one diol is a fluorinated diol.

Of course, as one of ordinary skill in the art would immediately recognize, mixtures of these diols, with or without additional diols known in the art, may also be used in forming the coated objects of the invention.

In a further preferred embodiment of the invention, the fluorinated polyols are synthesized by refluxing a mixture of diols 1 and 2 above with an equimolar amount of either diol 5 or diol 7 or a mixture of diols 3 and 4, with epichlorohydrin and an excess of sodium hydroxide in a solution of acetone containing a small amount of water. The reaction can be monitored by gas chromatography and reflux can be discontinued as soon the starting diols have disappeared. The resulting polyol can be washed with water until free of base and than dried at 120°C, producing a light amber solid in yields of 87 to 97%.

One of ordinary skill in the art would recognize that in the art of organic synthesis, many different synthetic protocols can be used to prepare a given compound. Thus the fluorinated polyols employed in the present invention can be synthesized by a variety of synthetic routes known to the skilled organic chemist. Different routes can involve more or less expensive reagents, easier or more difficult separation or purification procedures, straightforward or cumbersome scale-up, and higher or lower yield. The skilled chemist knows well how to balance the competing characteristics of synthetic strategies. Thus, the fluorinated polyols used in the present invention are not limited by the choice of synthetic strategy, as any synthetic strategy that yields a fluorinated polyol can be used.

An example of a suitable fluorinated polyol commercially available is a material sold under the trade name Poly-FOX by GenCorp Areojet of Sacramento, CA.

The fluorinated polyol is reacted with a curing agent in order to form the fluorinated polyurethane coating

Any urethane-grade solvents known in the art, such as those disclosed above, may be employed in the present invention.

The fluorinated polyurethane compounds may be employed in any amount that will desirably modify the surface properties of the coated golf ball. In particular, the fluorinated polyurethane compounds should be present in an amount sufficient to impart enhanced abrasion, impact and weathering resistance. If desired, a sufficient amount for imparting a decrease in the coefficient of friction may be applied.

Accordingly, the cured coating composition comprises about 1% to about 100% by weight fluorinated polyurethane. Preferably, the cured coating composition comprises about 10% to about 100% by weight fluorinated polyurethane. Most preferably, the cured coating composition comprises at least about 50% to about 100% fluorinated polyurethane. Preferably, the balance of the cured coating composition comprises a conventional, *i.e.*, non-fluorinated polyurethane. Any of the polyurethanes known in the art may be utilized. Polyurethane results from the reaction between a polyurethane prepolymer and a curing agent. The polyurethane prepolymer can be the product of a reaction between a polyol and a polyisocyanate. Curing agents such as polymines, glycols and diols can be used to cure polyurethane. A catalyst can be employed to promote the reaction between the curing agent and the polyurethane prepolymer.

Conventionally, there are two categories of polyurethane on the market, thermoset and thermoplastic. Thermostet polyurethanes are cured through crosslinking upon the substrate. Thermoplastic polyurethanes, on the other hand, are prereacted isocyanate and polyol or amine dispersed in solvent and cured through drying. Possible precursors for manufacturing thermoplastic and thermoset urethanes include, but are not limited to, 4,4'-diphenylmethane diisocyanate (MDI) or 3,3'-dimethyl-4,4'-biphenylene diisocyanate (TODI), and a polyol cured with a diol, such as 1,4-butanediol. In particular, thermoset polyurethanes are made from a

Accordingly, conventional polyurethanes can be made from any of numerous commercially available aromatic, aliphatic and cycloaliphatic isocyanates, diisocyanates and polyisocyanates.

The fluorinated polyurethane may be formed from a coating solution comprising a mix ratio of about 1:1 (OH to NCO). However, it may be preferable to have an excess of curing agent, i.e., NCO. Additionally, the coating solution may comprise between about 65% to about 80% by volume of a solvent. Preferably, the coating solution comprises about 10%-65% solvent.

In addition to the components discussed above, a variety of particulate materials may optionally be added to the coating compositions to modify the surface properties of the material. Any particulate materials conventionally employed in the coating composition art, such as pigments, dye, optical brighteners, flow agents, slip and mar agents, fillers, catalysts, mixtures thereof and the like may be utilized. For example, TiO_2 may be included as an opacifier or hiding pigment. Alternatively, or in addition, hard, abrasion resistant particulate materials such as silica particles may be added to the present coating compositions to enhance the abrasion resistance of the coating composition.

Additionally, due to the low surface energy of the present fluorinated polyurethane compositions, low surface tension particulate material may also be included. In particular, the surface energy of the fluorinated polyurethane compositions of the invention are comparable to that of poly(tetrafluoroethylene), sold commercially under the tradename Teflon®. Thus, a plurality of poly(tetrafluoroethylene) particles may be incorporated into the compositions to further enhance the durability and weathering, cleaning and surface friction reducing properties of the compositions used in coating the claimed objects.

It is preferable that the overall percentage by volume of the poly(tetrafluoroethylene) particles does not exceed about 38 percent in order to have a continuous film,

as a waterborne epoxy/acrylic/urethane resin system. However, solvent-based primer systems also may be used in the present invention. When a primer layer is employed, it is preferable that this layer be deposited prior to the application of the solution of the coating composition containing the fluorinated polyol. The primer layer is applied in such a manner as to result in a layer of uniform thickness. The viscosity and solids content of the primer layer can be adjusted by the addition of a suitable solvent such as water or any solvents known in order to facilitate its application to the ball. The primer layer can be deposited through any conventional application methods known in the art such as spray, dip, spin, electrostatic or flow coating methods. The primer layer should be allowed to air dry until tack-free before depositing the fluorinated polyol thereon, unless a wet-on-wet primer system is employed. Depending upon the material employed in, e.g., the golf ball cover, more than one primer layer may be required. For example, golf balls having a urethane or a balata cover may require two layers of primer.

The preferred thicknesses of the coating composition layer and optional primer coat layer(s) will vary depending upon the type of material to be coated. Nonetheless, the coating composition layer of the present invention should have a cured thickness of about 0.01 mils to about 3.0 mils. Preferably, the coating composition layer of the present invention has a cured thickness of less than about 2.0 mils.

When a primer layer is employed in the present invention, it should have a thickness of about 0.01 mil to about 1 mil. All thicknesses disclosed herein refer to the dry film thickness of each layer. Preferably, the primer layer is less than about 1.0 mil thick and the coating composition layer is less than about 2.0 mils thick.

As noted above, golf balls having a protective coating composition layer comprising the fluorinated polyurethane compositions described herein can have a reduced

An additional advantage of the presently claimed coating compositions results from the moisture absorption properties of fluorinated polyurethanes. Golf balls with a conventional polyurethane coating composition are known to absorb moisture after exposure to ambient atmospheric conditions over a period of time, resulting in a decrease in the velocity of the ball when struck with a club. This decrease in velocity is generally proportional to the decrease in the overall distance the ball travels when struck by a club. However, because of their low moisture absorption properties, the present fluorinated polyurethane coating compositions form excellent vapor barriers, thus decreasing the absorption of moisture into the core of the golf ball. Therefore, golf balls having the present fluorinated polyurethane coating compositions applied to their outer surface better maintain their initial velocity, and thus overall distance, as compared to conventional golf balls.

Likewise, as a result of their enhanced thermal and ultraviolet stability, the coating compositions used with the invention are more resistant to degradation due to exposure to elevated temperatures and/or ultraviolet radiation. The coating compositions of conventional golf balls degrade after being subjected to elevated temperatures for a prolonged period of time. Such degradation is usually manifested by a yellowing of the clear or white coating compositions, which is aesthetically unappealing and impacts negatively on the public perception of the overall quality of the golf ball. However, because of their excellent thermal and ultraviolet stability, the present fluorinated polyurethane coating composition compositions help prevent undesirable degradation as evidenced by yellowing.

The following is a representative example of a batch formulation for a fluorinated polyurethane coating composition of the present invention. However, it is to be understood that this example is provided only for illustrative purposes and in no way is the present invention limited to the specific disclosures therein.

CLAIMS

I claim:

1. A golf ball comprising a core, a cover and a coating composition layer deposited upon at least a portion of an outer surface of said cover, said coating composition layer comprising a fluorinated polyurethane resin.

2. The golf ball according to claim 1 wherein the fluorinated resin comprises a reaction product of a fluorinated polyol and a curing agent.

3. The golf ball of claim 2 wherein said curing agent is an isocyanate.

4. The golf ball of claim 2, wherein the coating composition layer comprises at least about 1.0 % by weight of said fluorinated polyurethane resin.

5. The golf ball of claim 2, wherein the coating composition layer comprises at least about 10.0 % by weight of said fluorinated polyurethane resin.

6. The golf ball of claim 2, wherein the coating composition layer comprises at least about 50.0 % by weight of said fluorinated polyurethane resin.

7. The golf ball of claim 1, wherein the coating composition layer additionally comprises at least one particulate material.

8. The golf ball of claim 7, wherein the particulate material comprises a plurality of poly(tetrafluoroethylene) particles.

9. The golf ball of claim 8, wherein said poly(tetrafluoroethylene) particles comprise less than about 38% by volume of said coating composition.

depositing upon at least a portion of an outer surface of said cover a coating composition layer formed by

(a) dissolving a fluorinated polyol in a solvent;

(b) reacting said polyol with a curing agent to form a reaction product;

(c) coating the surface of the golf ball with the reaction product.

18. The method of claim 17, which further comprises reacting at least two diols to form the fluorinated polyol;

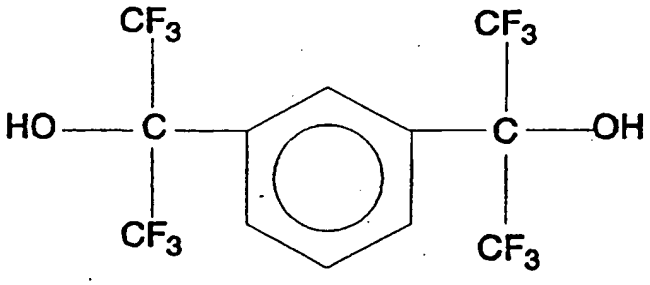
19. The method of claim 17, which further comprises:

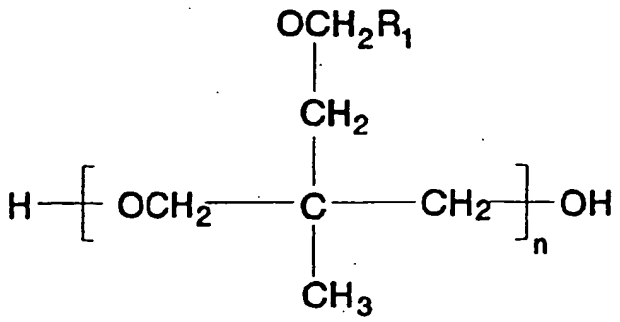
(a) dissolving the reaction product in a solvent to form a coating solution;

(b) depositing a layer of the coating solution upon substantially the entire outer surface of a golf ball; and

(c) curing the coating solution upon said golf ball surface.

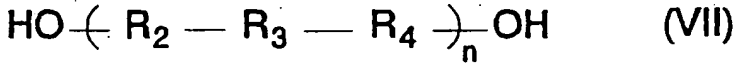
20. The method of claim 18 wherein said diols are selected from the group consisting of





(VI)

wherein $R_1 = C_nF_{2n+1}$; and



(VII)

wherein R_2, R_3 and R_4 are each selected from the group consisting of diols, with the provision that at least one diol is a fluorinated diol.

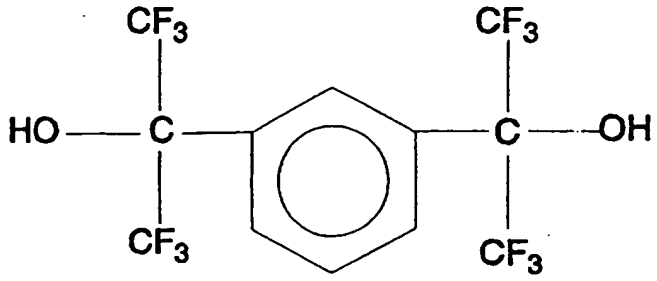
21. The method of claim 17, wherein the solvent is selected from the group consisting of methyl isobutyl ketone, methylamyl ketone, methyl isoamyl ketone or a mixture of *n*-butyl acetate and xylene.

22. The method of claim 17, wherein the method further comprises selecting an isocyanate as the curing agent.

23. The method of claim 17, which further comprises adding a particulate material to the reaction product to form an admixture thereof and thereafter dissolving the admixture in said solvent to permit deposition upon said ball surface.

24. The method of claim 23, which further comprises selecting said particulate material from the group consisting of poly(tetrafluoroethylene) particles, abrasion

29. The golf ball of claim 28 wherein said fluorinated diols are selected from the group consisting of;



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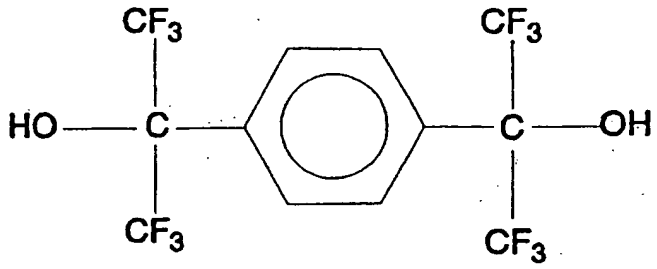

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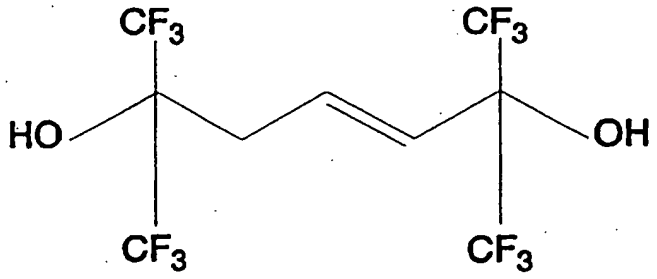

30. The golf ball of claim 27, wherein the curing agent is an isocyanate.